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SPIN-LATTICE INTERACTION IN THE CUBIC SYSTEM V^{3+}:CaF_2

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The spin-lattice coupling constants for a V^{3+} impurity ion in fluorite were determined by the uniaxial pressure technique. The elements of the coupling tensor, representing the splitting of the spin levels during lattice deformation, were: $G_{11} = -1.2\ \mathrm{cm}^{-1}$, $G_{44} = 7.4\ \mathrm{cm}^{-1}$. The tensor elements related to the variation of the hyperfine interaction were $Z_{11} = 0.03\ \mathrm{cm}^{-1}$, $Z_{44} = -0.18\ \mathrm{cm}^{-1}$. The spin-lattice relaxation time calculated for direct processes (~0.05 sec) differed considerably from the values observed at helium temperatures.

ZARIPOV et al.[1] discovered an isotropic EPR spectrum of trivalent vanadium ions in CaF_2. The ground state of V^{3+} ($3d^2\ {}^3F$) in a cubic field, which is an orbital singlet, is triply degenerate in spin (S = 1). One would expect the axial component of the crystal field, which would appear on the application of an external uniaxial pressure, to split the EPR lines in the same way as in the well-known case of Ni^{2+} ($3d^8\ {}^3F$) in MgO.[2] Comparison of the data on the splitting of isotropic EPR lines by the actual distortion of the oxygen octahedron and the fluorine cube may be useful in the theory of crystal fields. The purpose of the investigation reported here was to determine the spin-phonon coupling constants of V^{3+} in CaF_2.

THEORETICAL RELATIONSHIPS

As is usual for the iron-group ions having spins $S > 1/2$, the spin-phonon interaction Hamiltonian is represented in the form which is quadratic in spin variables and linear in deformations. We shall write this Hamiltonian in the form of two terms, representing changes in the electron and electron-nuclear levels:

$$\mathcal{H}' = \sum_{i,k,l,m} \frac{1}{2}[(S_iS_k + S_kS_i)G_{iklm} + (S_iI_k + S_kI_i)Z_{iklm}]u_{lm}; \quad i,k,l,m = x,y,z, \tag{1}$$

where $u_{lm} = (1/2)(\partial u_l/\partial x_m + \partial u_m/\partial x_l)$ is the deformation tensor. If x, y, and z are made to coincide with the fourfold axes, the Hamiltonian of Eq. (1) transforms into

$$\begin{aligned}\mathcal{H}' = {}^3/_4G_{xxxx}\{[S_z^2 - {}^1/_3S(S+1)](2u_{zz} - u_{xx} - u_{yy}) \\ + (S_x^2 - S_y^2)(u_{xx} - u_{yy})\} + 2G_{xyxy}[(S_xS_y + S_yS_x)u_{xy} \\ + (S_xS_z + S_zS_x)u_{xz} + (S_yS_z + S_zS_y)u_{yz}] \\ + {}^3/_4Z_{xxxx}[(S_zI_z - {}^1/_3\mathbf{SI})(2u_{zz} - u_{xx} - u_{yy}) \\ + (S_xI_x - S_yI_y)(u_{xx} - u_{yy})] + 2Z_{xyxy}[(S_xI_y + S_yI_x)u_{xy} \\ + (S_xI_z + S_zI_x)u_{xz} + (S_yI_z + S_zI_y)u_{yz}].\end{aligned} \tag{2}$$

Here, G_{xxxx}, G_{xyxy} and Z_{xxxx}, Z_{xyxy} (or G_{11}, G_{44} and Z_{11}, Z_{44}) are two independent components of the G and Z tensors, which are retained after applying the symmetry conditions and the condition Sp $\mathcal{H}' = 0$.

In two special cases, when $P \parallel C_4$ and $P \parallel C_3$, these components can be separated so that the conditions $u_{xy} = u_{xz} = u_{yz} = 0$ and $u_{xx} = u_{yy} = u_{zz}$ are satisfied, respectively. In these two cases of the tetragonal and trigonal distortions of the cubic symmetry field, the splitting of the lines can be easily calculated by the perturbation theory method and the final results have the following form (the magnetic field is assumed to be perpendicular to the direction of pressure):

$$\begin{gathered}(\Delta H)_{\text{tety}} = \frac{3}{2}G_{11}u - \frac{9A^2}{4H_m^2}[I(I+1) - m^2]G_{11}u \\ - \frac{mA}{2H_m}Z_{11}u + \frac{m}{2H_m}Z_{11}^2u^2, \\ u = (s_{11} - s_{12})P,\end{gathered} \tag{3}$$

$$\begin{gathered}(\Delta H)_{\text{trig}} = 6G_{44}u - \frac{9A^2}{H\ \ 2}[I(I+1) - m^2]G_{44}u \\ - \frac{2mA}{H_m}Z_{44}u + \frac{8m}{H_m}Z_{44}^2u^2, \\ u = {}^1/_3s_{44}P,\end{gathered} \tag{4}$$

where s_{ik} are the elastic constants; P is the external pressure; A is the hyperfine structure constant; H_m is the resonance value of the magnetic field for the component of the spectrum corresponding to the projection of a nuclear spin m.

EXPERIMENTAL RESULTS

We used the method described in[3] for investigating EPR in the presence of an external uniaxial pressure. The measurements were carried out at 4.2°K at a frequency of 9.4 Gc.

The EPR spectrum of V^{3+} in the lattice of CaF_2 consists of eight isotropic components of the hyperfine structure of the main isotope V^{51} (I = 7/2). The parameters of the spin Hamiltonian are: $g = 1.933 \pm 0.005$ and $|A| = 263 \pm 2$ Mc.[1] Each component of the hyperfine structure is a doublet since, in the first approximation, the electron transitions with ΔM ($0 \rightarrow \pm 1$), $\Delta m = 0$ are identical. Corrections in higher approximations in respect of the hyperfine structure shift these transitions relative to one another by an amount $(\delta H)_m$, which is manifested experimentally by differences in the widths of the spectral lines. Since the influence of pressure is to split the lines of the spectrum and its effect is not very large, it is necessary to make corrections for the doublet structure of the components. The relationship for the difference between the values of the resonance fields of the transitions $(1 \rightarrow 0, m)$ and $(0 \rightarrow -1, m)$ can be obtained, with third-approximation accuracy, using the results of Zaripov et al.[4] This difference is given by

$$(\delta H)_m = \frac{A^2}{H_m}\left\{-m + \frac{A}{H_m}[3m^2 - 2I(I+1)]\right\}. \tag{5}$$

The sign of $(\delta H)_m$ and the signs of the experimentally determined splittings and of the spin-coupling constants are all governed by the sign of the parameter A. All subsequent results will be based on the assumption that $A > 0$. The values of $(\delta H)_m$ are given in the caption of Fig. 1. In our analysis of the experimental data, we shall use the values of $(\delta H)_m$ obtained by solving the matrix of a 24-th order secular equation using an electronic computer; these values differ, on the average, by 10% from the third-approximation results.

We shall consider first the experimental results obtained under a pressure directed along a fourfold axis of a crystal. Using a pressure of 5.28×10^8 dyn/cm^2, we measured the splittings of four weak-field lines in the spectrum ($m = 7/2, 5/2, 3/2, 1/2$), since the two next lines were not resolved and the lines with $m = -5/2$, $-7/2$ exhibited definite narrowing. This behavior of the spectrum can be understood by the examination of Fig. 1. The sign of the splitting of ΔH is, in this case, negative. The splitting pattern of three weak-field lines is shown in Fig. 2 and the results are given in Fig. 3 of measurements that take into account $(\delta H)_m$. It is evident from this figure that the pressure-induced splittings are small: ~10 G.

Different results were obtained for $P \parallel C_3$. In this case, the influence of the pressure was considerably stronger and the splitting pattern changed as follows. At moderate pressures, each of the spectral lines split into three components: a strong central component and two weak side lines. The ratio of the intensities of the central and side components was ~6 : 1. At pressures higher than 300 kg/cm^2, the central line split again into several components and the spectrum became very complex. This effect can be explained in a natural manner by assuming the presence of a small trigonal distortion D_0 in the environment of V^{3+}, i.e., the presence of four magnetically and elastically inequivalent ions. In this case the lines of a complex with orientation is $C_3 \perp H$, $C_3 \parallel P$ move most rapidly out of the general group of lines. The lines of the other three complexes, which experience deformations of opposite sign and lower magnitude, are shifted in the opposite direction and are split (at sufficiently high pressures) into four or six lines, depending on the magnetic field orientation. We note that the presence of the trigonal distortion is also in agreement with the observation of a considerable narrowing of the lines of the spectrum when $H \parallel C_4$.

The results of the measurements of the splitting for two values of pressure are given in Fig. 3.

CALCULATION OF SPIN-LATTICE INTERACTION CONSTANTS

Equations (3) and (4) contain terms which depend on m^2 but, since they are much smaller than the other terms, the experimental results should be analyzed using the least-squares method in the linear approximation with respect to m (Fig. 3). Dependences 1 and 2 in Fig. 3 allow us to determine the value of D_0. In fact, if we substitute $m = 0$ in Eq. (4), we find that the ratio $\Delta H_1/\Delta H_2$ at this point should be equal to the ratio of the corresponding pressures P_1/P_2. This condition is satisfied if the value $D_0 \approx 8$ Oe is subtracted from the experimental data. The agreement of the sign of D_0 with the sign of the splitting, produced by the application of

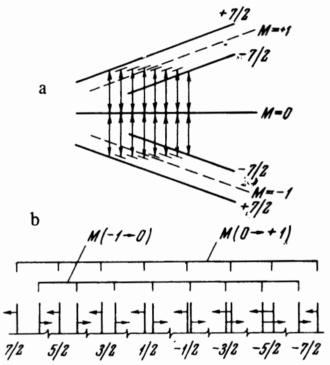

FIG. 1. Effect of pressure on the EPR spectrum of V^{3+} in CaF_2: a) energy level scheme of V^{3+} in a strong magnetic field, taking account of nuclear spin ($A > 0$) but neglecting higher-approximation corrections; b) EPR spectrum of V^{3+} in CaF_2 with an internal structure of the hyperfine components. The values of $(\delta H)_m$, calculated from Eq. (5) are (in G): – 10.7; – 9.1; – 6.6; –4.2; –1.1; 2.2; 5.8; 9.6. The arrows indicate the direction of the shift of the lines for $P \parallel C_4$. The direction of the shift is opposite for $P \parallel C_3$.

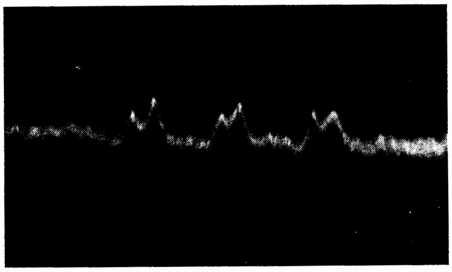

FIG. 2. Oscillogram of the spectrum for $P \parallel C_4$, $H \perp P$, $m = 7/2, 5/2, 3/2$.

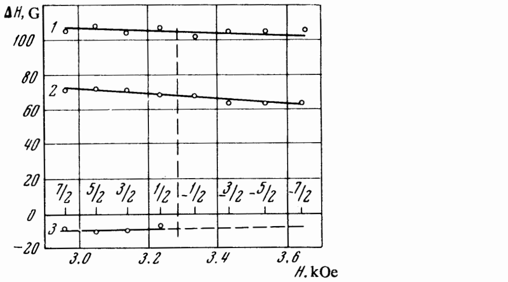

FIG. 3. Experimental results (for $H \perp P$): 1), 2) splitting of the spectral lines in the trigonal distortion case under pressures of 2.14×10^8 and 1.34×10^8 dyn/cm^2, respectively; 3) splitting in the case of the tetragonal distortion and $P = 5.28 \times 10^8$ dyn/cm^2.

Table II

Lattice	Ion	G_{44}, cm^{-1}	Calculated [11] TT_{1d}, sec. deg K	Measured TT_1 sec. deg K	TT_{1d} calculated from Eq. (6), sec. deg K
MgO	Cr^{3+}	+4.2	0,65; 0,33	1,1	1 8
	Mn^{2+}	—0.27	2.5; 1,3; 0.39	2	160; 64
	Fe^{3+}	—0.72	0.21; 0,11; 0.03	3; 0,1	22.2; 8.9
	Fe^{2+}	+540	$1.1 \cdot 10^{-4}$	$6 \cdot 10^{-4}$	$6.6 \cdot 10^{-4}$
	Ni^{2+}	+36	$8.5 \cdot 10^{-3}$	—	$143 \cdot 10^{-3}$
CaF_2	V^{3+}	+7.4	$2.5 \cdot 10^{-3}$ [7]	$9 \cdot 10^{-3}$	0.1

a pressure along the C_3 axis, indicates that the trigonal distortion is due to the displacement of fluorine ions along one of the space diagonals of a cube along direction toward an V^{3+} ion. Comparison with the results obtained under pressure indicates that this shift is about 1.6×10^{-4} Å.

Using the obtained value of D_0 and $s_{44} = 2.781 \times 10^{-12}$ cm^2/dyn,[5] we obtain from Eq. (4) the value $G_{44} = 8.16 \times 10^4$ G. Similarly, the constant G_{11} is calculated directly from the results in Fig. 3, since D_0 does not influence the results obtained with $H \parallel C_4$. Using $s_{11} = 0.682$, $s_{12} = -0.166$ (expressed in units of 10^{-12} cm^2/dyn),[5] we obtain $G_{11} = -1.36 \times 10^4$ G.

Generally speaking, the values of Z_{11} and Z_{44} can be calculated from the angular coefficients of the experimental dependences. It is evident from Fig. 3 that the slopes of the straight lines depends on the value of the pressure, which is explained qualitatively by the competition of the last two terms in Eq. (4). Quantitative calculations using Eq. (4) overestimate the values of Z_{11} and Z_{44}, for which the change in the hyperfine structure constant under the application of pressure would have to be ~20%. Therefore, these quantities should be calculated from direct measurements of the value of A, which, in the first approximation, varies in accordance with the relationships $A_{tetr} = A - (1/2)Z_{11}(s_{11} - s_{12})P$ and $A_{trig} = A - (2/3)Z_{44}s_{44}P$. These measurements give the following values of the Z tensor components: $Z_{11} = 3.6 \times 10^2$ G, $Z_{44} = -2.02 \times 10^3$ G. The results are summarized in Table I.

COMPARISON WITH RELAXATION DATA

Calculations of the probability of a transition in direct processes, using the Hamiltonian of Eq. (2) as a perturbation, give a fairly cumbersome general expression which simplifies for the normal transitions $\Delta M = \pm 1$, $\Delta m = 0$, in which we are interested:

$$\frac{1}{T_{1d}} = \frac{32}{15}\,\frac{\pi^3 \nu^3}{h\rho}\left(\frac{1}{v_l{}^5} + \frac{3}{2v_t{}^5}\right)\cot\left(\frac{h\nu}{2kT}\right)\left(|G_{44}\langle M|S_xS_z + S_zS_x|\mathrm{M}-1|\rangle + Z_{44}\langle M,m|S_xI_z|M-1,m\rangle|^2\right), \tag{6}$$

where ν is the frequency of the transition; ρ is the density of the crystal; v_l and v_t are the velocities of longitudinal and transverse acoustic waves.

In the derivation of this formula, we have taken into account the dependence of the velocity of propagation of vibrations due to the polarization and we have made a rigorous allowance for the angular components which appear in the calculation of the matrix elements of the lattice deformation.[6] The expression given in Eq. (6) differs by a factor ~1/20 from other known formulas (cf., for example, Karlov and Manenkov[7]), i.e., in those cases when allowances for the factors included in our expression are not made, the probability of a transition is overestimated by more than one order of magnitude. For this reason, contradictory results are frequently obtained. Thus, in a summary table in Jeffries's book,[8] which gives the results of experiments on the iron-group ions in MgO, the calculated relaxation times for all ions are found to be smaller (!) than those observed experimentally. Part of Jeffries's table is reproduced in our paper, in addition to the results of calculations using Eq. (6) and the results for V^{3+} in CaF_2 (Table II). In our calculations concerning MgO, we have assumed that $v_l = 9.0 \times 10^5$ cm/sec, $v_t = 6.68 \times 10^5$ cm/sec,[9] $\rho = 3.58$ g/cm^3, $\nu = 9.4$ Gc.

Assuming that, for CaF_2, $v_l = 7.36 \times 10^5$ cm/sec, $v_t = 3.34 \times 10^5$ cm/sec, $\rho = 3.21$ g/cm^3,[10] $\nu = 9.4$ Gc, $T = 2$°K for transitions with $m = 7/2$ and $m = -7/2$, we obtain values of 0.06 and 0.04 sec, respectively, for T_{1d}. It is known from the experimental data that V^{3+} in CaF_2 relaxes more rapidly. The relaxation times observed experimentally under the same conditions are equal for all lines in the spectrum and they amount to 4—5 msec (the results obtained by R. M. Valishev and I. N. Kurkin) and, obviously, these relaxation times are not due to pure Van Vleck processes.

Table I. Coupling constant of V^{3+} in CaF_2 (cm^{-1}).

G_{11}	G_{44}	Z_{11}	Z_{44}
-1.2 ± 0.15	7.4 ± 0.06	0.03 ± 0.02	-0.18 ± 0.03

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12